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WOODS HOLE, MASSACHUSETTS

WOODS HOLE OCEANOGRAPHIC INSTITUTION
Woods Hole, Massachusetts

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Hydrographic Survey in the Boston-Area

Organic Content and Its Significance in the Sediments

Prepared by John T. Conover

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Director

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INTRODUCTION

As part of the Inshore Survey program in Boston Bay, samples for an analysis of organic content were removed at certain levels from Kullenberg cores. The coring operations were conducted from the R/V CARYN during the weeks of April 29, 1952 and May 12, 1952, inclusive (W.H.O.I. Ref. No. 52-56). Other reports concerned with this program from which data were used for the present study, are the following: W.H.O.I. Ref. Nos. 53-15, and 53-17.

The purpose of obtaining values for organic content in bottom sediments was: (1) to add to the information yielded by mechanical analysis; (2) to study the occurrence of higher values of organic content in some limited areas; and (3) to study the relationship between organic content and the frictional and cohesive qualities of sediments.

ANALYTICAL METHODS

The chromic acid reduction method for an analysis of organic content in soils (Allison, 1935) was used as directed by instructions in the "General specifications for the individual area covered by Inshore Survey contractors", enclosure in Hydrographic letter code 46-GJ/eb ser. 863, dated April 7, 1952. Some minor modifications of the wet combustion method were employed and additional analyses for contaminants were made to adapt the method to marine sediments; otherwise the Allison schedule was followed in detail.

Sampling and Preparation: As stated in an earlier report (W.H.O.I. Ref. No. 52-56), two and one-quarter inch sections were removed from 67 cores usually at two foct intervals. The sample was removed with a teaspoon from certain horizons of the core, but no attempt was made to secure the entire diameter of the plug at the particular horizon chosen. It is possible that the sample is not representative of that horizon. The sample should have included the entire diameter of the plug section to obtain as representative a sample as possible.

Following a rigidense measurement, enough material was removed to fill a two ounce shell vial. Five drops of chloroform were added just before sealing the vials. Some microbial

* The vials should have been rinsed out with chloroform before adding the sample to assure good penetration of the bactericidal reagent. Drying should be delayed as little as possible. Very fluid, watery-silt samples should be put up in eight ounce quantities to provide enough sediment for analysis.

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activity probably occurred in the samples during the four to six weeks storage period prior to drying in an oven. The samples were oven-dried at 85° to 90°C (waksman, 1929, 1933) for four days until thoroughly dry, and then stored in a desicator until wet combustion analysis was begun. The organic content analysis was begun October 28, and completed by December 17, 1952.

Vials containing the samples were again oven-dried at 90° for four days, just prior to analysis, to bring them to constant weight, and then cooled in a freshly charged desiccator. The entire contents of each vial in turn was removed, placed in a mortar, and ground with a pestle until as much as possible of the sample had been reduced to less than 100 mesh. Coarse fragments of quartz, felspar, and other granitic materials were removed from the sample, as only the finer fractions of a sediment have been shown to contain residues of organic material (Twenhofel, 1950; Trask, 1942). Fragments of coal were also removed, but were weighed and expressed as a per cent of the total sample weight. It is assumed that the source of such coal is industrial and not netural to the sediments of the Boston area (La Forge, 1932). The amount of coal or slag present was relatively slight, as only two samples out of the 157 were so contaminated, and these were from the uppermost layer of sediment.

The 100 mesh samples were carefully mixed on a plastic or waxed paper sheet in accordance with the technique recommended by Scott (1939). Each corner was lifted in turn at least 50 times before weighing out a 0.5 gram sample for analysis. Samples were run in duplicate. All values represent averages from titers of duplicate runs. It was found that samples run in duplicate without mixing often gave a spread of 5% to 6% deviation in the titer. Mixing generally gave duplicate titers less than 2%. It was impossible to mix, representatively, fractions larger than 100 mesh with those smaller. Only the smaller fractions entered into the actual analysis. However, it is assumed that all significant amounts of organic matter in a sample were measured in the analysis. The total weight of inorganic material was slightly lower than that actually represented in the field sample. It is suggested that entire samples be ground in a mill which will reduce the sample to less than 100 mesh.

After drying to constant weight, mixing, and weighing critically, the 0.5 gram samples (or fractions thereof if insufficient sediment was available) were carefully brushed with a good quality, artists, shedless, semi-soft brush into heavy-walled, pyrex ignition test tubes (200 mm x 25 mm o.d.) containing pre-oven-dried 0.1 N potassium dichromate solution.

Just prior to digestion, 10 cc of 95.5 per cent sulfuric acid were added. (It is important that only glass comes in contact with the acid in setting up a dispensing unit). A further refinement for marine sediments not employed in the present analysis, recommended by Southward (1952), is the addition of 25 gms silver sulfate to each liter of acid.

Digestion of the Sample: The accuracy of the analysis depends largely upon the care employed in heating the digest. The Allison-Schollenberger method requires that the digest sample be brought up to 175° within a period of 90 seconds and immediately upon reaching this temperature be allowed to cool in air for 5 minutes before attempting to chill further with running water. Following this technique duplicate samples rarely gave less than 5% deviation from their average. In an experimental run using a single sample, digests were allowed to remain at a temperature of 175°C for a period of 30 seconds in addition to the usual time schedule. Constant temperature was achieved plus or minus 0.5°C. by passing a 3 cm high flame from the microburner across the bottom of the ignition tube at two second intervals. In practice this technique showed no appreciable increase in average values of the reduction oxidation processes in the analysis but the deviation between the titer of two samples was usually below 2% (Fig. 1, Table 1). The digest time was extended to a total of 120 seconds, 90 seconds to reach 175°C and 30 seconds duration at 175°C, in the analysis carried out in this laboratory for the Boston Bay sediments.

Preparation of the Digest for Titration: After diluting the digest to 150 cc with distilled water, the sample solutions were permitted to stand for exactly 30 minutes before titrating. If a sample solution was allowed to stand for more or less time than that given in the Allison schedule, the amount of titer varied accordingly. If sodium fluoride salts, followed by the indicator (barium diphenylamine sulfonate was used because it gave sharp end points), were added immediately prior to titration, no trouble was experienced, but if added even as much as two or three minutes before titration was begun, results were more variable. Apparently time is a very important factor to consider if reproducible results are desired. Errors may also be caused by excess potassium dichromate becoming trapped on undissolved grains of sodium fluoride.

Computations: Computations were made in accordance with the Allison-Schollenberger method using the following formula:

% of organic carbon = $\frac{100 \text{ x } \triangle \text{ml. x normality of Fe(NH₂)(SO₄)₂ x .3456}}{\text{weight of sample}}$



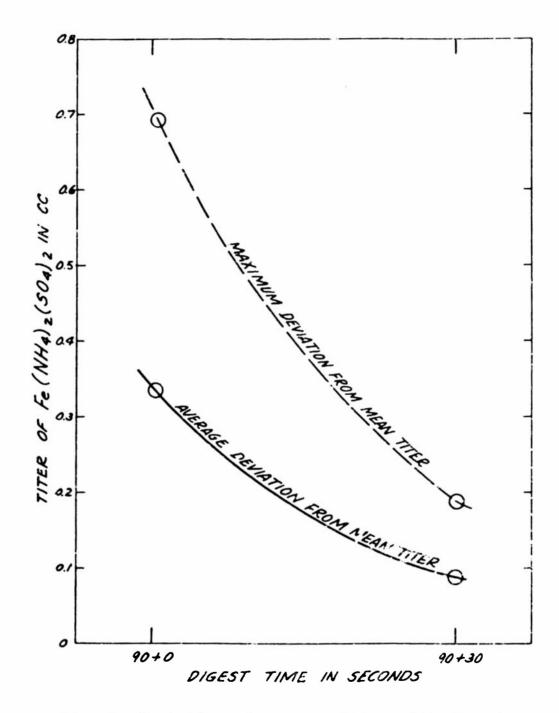


Fig. 1 Deviations from mean titer with digest time showing improved titration accuracy with an increase of 30 seconds at constant temperature

Data from a digest time run

Table 1

Titer in cc after 90+0 seconds	Dev.	af	ter in cc ter 90+30 econds	Dev.
13.95 14.10 13.15 13.05 13.40 13.50 13.65 13.05 13.10 12.95 13.80 13.00	0.56 0.71 0.24 0.34 0.01 0.11 0.26 0.34 0.29 0.44 0.41 0.39		13.25 13.10 13.05 13.20 13.10 13.15 13.00 13.30 12.95 13.00 13.10	0.12 0.03 0.08 0.07 0.03 0.02 0.13 0.17 0.17 0.18 0.13 0.03
13.39	0.34	means	13.13	0.1

Maximum in test	deviation run	0.71	cc	Maximum in test	deviation run	0.18	cc
Maximum in pract	deviation tice	1.5	cc	Maximum in pract	deviation tice	0.50	ce

where \triangle ml. is the titer difference between sample and blank, and 0.3456 is a constant including the Schollenberger constant multiplied by the milliequivalent weight of carbon.

Comments on the Preparation of Reagents: Following some experimentation it was found unnecessary to use a Kipp hydrogen generator to keep the ferrous ammonium sulfate stable. The solution was made up 4 liters at a time in a 5-liter brown bottle to which an automatic burette was connected. The air intake line was stoppered off when the burette was not in use. An equilibrium between the carbon dioxide in the atmosphere over the reagent was apparently reached in a few days and the normality of the solution, checked twice daily, decreased on the average of .00083 N per day over a period of two weeks during which time the supply was exhausted. When the concentrated sulfuric acid content of the ferrous ammonium sulfate, as described in the Allison schedule, is raised from 20 cc to 40 cc per liter, a drift in normality of .00031 per day was observed (Table 2).

If silver sulfate solution is employed to take up the chloride in the analysis it should be added to the stock supply of concentrated sulfuric acid used to prepare the sample for digestion.

During standardization of the ferrous ammonium sulfate solution with potassium dichromate solution, sharper end points could be obtained if 10 cc concentrated sulfuric acid diluted with 150 cc of cold distilled water and cooled to room temperature, is added to the solution just prior to titration.

Total Organic Content Analysis: Organic content of 8% of the samples was determined by the loss of weight on ignition at 600°C for 2 hours. After drying samples in their original vials for 4 days at 90°, the vials were stoppered and placed in a desiccator to cool prior to weighing. Samples were removed quickly to porcelain crucibles predried for 1 hour at 600°C; the vials were then reweighed for the preignition weight of the sample. In this manner, error from moisture adsorption was minimized. Dried marine sediments are extremely hydroscopic. The crucibles containing the samples were then placed in an electric oven for 2 hours at 600°C, cooled in a desiccator, and weighed. Pairs of duplicate samples were ignited and the weight losses averaged.

Total Extractable Iron Analysis: Total iron was analyzed by the use of Knop's modification of Penny's method (Knop, 1924; Penny, 1850). Samples were first prepared (and ignited as described above) to eliminate the carbon prior to digestion.



Table 2

Drift in normality of the ferrous ammonium sulfate solution without a hydrogen atmosphere

	- 10 100	
Normality	Date Checked	Average Daily Change
.236 .235 .233 .231	Nov. 14) Nov. 17) Nov. 21) Nov. 24)	.0008 N 20 cc H ₂ SO ₄ /L
. 240 . 240 . 238 . 238 . 237 . 235	Nov. 26) Dec. 1) Dec. 3) Dec. 8) Dec. 9) Dec. 10)	.00031 N 40 cc H ₂ SO ₄ /L

Table 3

Results of total extractable iron analysis on some of the sediment samples from Boston Bay

Station-Core	Type	Depth from	Possible	% Organic	% Total	% Maximum Possible	
Number	Sediment	Top of Core	Age	Carbon	Iron	Error Due to Iron	
226B 226B 219A 148B 208A 184A 163A 166A	Silt Clay Silt Send Silt Silt Clay Silt	21 41 01 01 01 01 01 01	Recent Glacial Recent Recent Recent Recent Recent	0.343 0.357 3.65 2.98 2.24 4.09 1.83 5.13	0.19 0.58 0.40 0.311 0.304 0.451 0.47	0.0117 0.036 0.025 0.019 0.019 0.028 0.029 0.027	

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CRITIQUE OF THE ORGANIC CARBON ANALYSIS

The Allison method is not directly suited to an analysis of organic carbon in marine sediments, but requires some modifications to obtain reproducible results. The modifications used in the present study have been described under sample preparation and digestion.

In the analysis, according to Emery and Trask, free carbon is not oxidized, and carbonate carbon is not included. Therefore it is presumed that organic carbon is determined. The method has been criticized by Emery and Trask (Emery & Rittenberg, 1952; Trask, 1942) who agree that high values of carbon will be obtained for highly reduced organic materials. It is improper to assume that all samples of that sediment are at the same state of reduction, despite their depth in the environment. Emery (Emery & Rittenberg, 1952) states that it is not an absolute method because such an assumption is false. Trask (1942) recognized this fact and used the Schollenberger method to obtain what he called a "reduction number", which was used as a rough index of the degree of reduction in marine sediments. Emery (Emery & Rittenberg, 1952) has gone a step farther end used values obtained with the Allison method to evaluate the state of reduction in a sediment by comparing the difference between such values and those determined by the Waksman-Starkey combustion method which measures the weight of carbon dioxide liberated (Waksman & Starkey, 1923). Large differences between results of the two methods indicate a high state of reduction of the organic matter.

In this study the independent carbon determinations are not available to permit the calculation of reduction by the method of Trask or Emery. The above limitations of the method must be considered in evaluating our "carbon" values.

Reliability of the Method: To test the reliability of the Allison-Schollenberger method as applied to marine sediments, the carbon determination by the method was compared to the loss on ignition at 600°C for 8% of the samples analyzed. Most organic carbon values were between 37% and 44% and averaged 41.9% of the total organic matter. Dirferences between duplicate determinations for organic carbon averaged between 0.05% and 0.15% of the total sample weight, the differences increasing with carbon content. This error reflects only the degree of reproducibility and does not imply deviations from an absolute value for organic carbon.

Tests for Contaminants: A limited inquiry into the affects of coal and iron on the Allison method was made and the amount of interference determined.



Coal: Contrary to Emery's (Emery & Rittenberg, 1952) contention that free carbon is not oxidized, samples containing grains of coal gave considerably higher values for carbon than those same samples with the coal removed. The two samples which contained coal fragments were cleared of the contaminant before the Allison method was employed. Southward (1952) also found that coal affected the method.

Iron: It was noticed that some semples had shown a rusty color upon exposure to air for a few days suggesting the presence of some iron in the sediments. Some samples from cores exhibiting this color change also had higher organic content values. As the amount of pyrite is known to affect the reduction of organic matter in situ, and could also interfere with the Allison method, iron analysis was made on some of the samples and the results are presented in Table 3.

The highest concentration of iron was 0.58%. It is computed that this proportion of iron would be equivalent to 0.036% organic carbon if it reacts completely in the Allison method. The organic carbon determined in this particular sample was 0.35%. If all of the iron is involved in the reaction, the correct carbon value should be 0.393 if all ferrous iron were present, or 0.321% if all ferric iron were present.

The absolute error for the presence of iron was determined by comparing the milliequivalent of potassium dichromate in terms of iron and carbon.

If the per cent iron =
$$\frac{\Delta \text{ ml. } \text{Cr}_2 \text{ } 0_7 \text{ x } \text{ (n) } \text{Cr}_2 \text{ } 0_7 \text{ x } 55.84 \text{ x } 100}{\text{weight of sample x } 1000}$$

and

If the per cent organic carbon
$$\frac{\triangle ml. Cr_2 O_7 \times (n) Cr_2 O_7 \times 0.3456}{\text{weight of sample}}$$

then the maximum possible error due to iron as it affects the per cent of organic carbon determined by the Allison method can be found by substitution in the following combined expression:

The iron content of the sediment samples analyzed was low enough so that this degree of iron interference should not be significant. If the amount of iron were in excess of 1%, serious error would result, especially for the low values

of organic carbon obtained in the survey. Scuthward (1952) found that iron in excess of this amount could alter the results of the method. Trask (1942) attempted to eliminate this problem by passing a magnet through the sediment to remove traces of pyrite. Perhaps following such a technique, an iron analysis could be run and if no significant quantities were present one could employ the Allison method.

Salt: No correction was made for salt error. Trask (1942, p. 57) deduced that although the concentration of sodium chloride could affect the Allison method, the salinity of the surficial sediments in the marine environment was usually that of the bottom water (in Boston Bay this value is appreximately 31 %) which contributed less than 0.20% error to the Schollenberger method. Such a magnitude of error would affect the results, but assuming that all values for organic carbon are so affected by nearly the same concentrations of salt, the error would not be detectable.

RESULTS

Establishing a Constant to Compute Organic Content from Organic Carbon: As the purpose of the analysis was to obtain a value for organic content in situ, an attempt was made to relate organic carbon values to total organic content. The total organic content in soils and sediments for many years in the past has been expressed as the weight loss on ignition (Waksman, 1933; Trask, 1942). With care, loss of weight on ignition can yield reproducible results, provided the sample is guarded against the adsorption of moisture. Using the weight loss values from the ignition experiment and the values for organic carbon obtained by the Allison-Schollenberger method, an average organic carbon value of 41.9% of the total organic content was obtained from 14 samples, with the extremes represented ranging from 32.8% to 60.2% but the majority falling between 37% and 44%. To obtain all organic content values for the inshore project in the Boston Harbor, all organic carbon values were multiplied by the 2.29, a constant derived from the median organic carbon value of 41.9%. This constant is large in contrast to those computed by Trask, 1.7 (1942), Waksman, 1.887 (1933), and Boysen-Jensen, 2.0 (1914), and implies that the amount of carbon recovered in the Boston Bay sediments is somewhat lower than that computed for sediments analyzed by the above investigators.

waksman (1933) studied the superficial sediments of Buzzards and Cape Cod bays, Massachusetts, which are similar to those in the Boston Harbor area in that these bays are also underlain by ground moraine. He used a dry combustion method, obtained total carbon values, employed an extraction technique, established the percentage of organic carbon to inorganic carbon, and then computed the average organic carbon to total organic centent to be 53%, giving a constant of 1.887. These same

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The relationship between organic earbon and total organic content computed by loss of weight on ignition

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- 0		_ 28	•	20	40	0 2/
1 L		1000	3	C .	· ·	Ea
- 0	Type Sediment	Depth f		Organ Post	Total Ranic	Organic Organic
Stat1e Number	6-	20	Possi	2.0	00	62
£ 5	- 50	65	5 80	20	25	4.
₩ Z	E 20	35	24	W6.0	160	46 0
226B	Silt	51	Recent .	0.343	1.05	- 32,8 -
219A	Silt	0 -	Recent	3.65	. 3.65	45.8
148B	Send	0.51	Recent	3.65	4.10	760.8 -
208A	Silt	01	Recent	2.24	6,23	142/8
184A	Silt	01	Recent	4.09	0-53	12.7
163A	Clay	01	Recent	1.83	4.20	43.5
166A	Silt	01	Recent	5.13	12.92	13.5
2340	Clay	41	Glacial	5.13	3.92	37.6
234B	Clay	21-	Glacial	0.894	2.04	13.8
243B	Sand	21	Recent	0.452	1.14	39.6
221A	Clay	01	Recent	2.62	6,20	42.4
216B	Silt	41	Glacial	1.0	2.48	Ho.li
194C	Sand	4'	Glacial	0.5	1.36	37-4
184A	Silt	ð1	Recent	4.09	19.74	42.0
<i>f</i>					f	

/ mean = 41.9%

* Obtained by noting the loss of weight by ignition.

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samples were also analyzed by Waksman for loss of weight on ignition (Table 5). If computed for the percentage of organic carbon using his loss of weight on ignition as total organic content, the ratio of organic carbon to total organic content is 34.6%. The average value for organic carbon in the Boston Harbor survey is not far removed from that computed from Waksman's data using his loss of weight on ignition as total organic content (Fig. 2, Buzzards and Cape Cod Bays No. 2, and Table 5).

It is of interest here that Allison criticized Waksman's extraction method as being too variable and untrustworthy (Allison, 1935). Apparently there is no really satisfactory means of analyzing organic content available. Trask (1942) admitted that one could not establish such relationships within less than 5 to 10% of the absolute value with methods available in 1942. Emery (Emery & Rittenberg, 1952) comments on this state of affairs as having changed but little. He used Trask's constant in his computations for organic content.

Either an erbitrary constant based upon unsupported assumptions must be chosen, or, one should be computed from the specific sediments under analysis. The latter choice is the better alternative as long as values for organic content using those constants most commonly employed are also given for additional reference (Table 6).

After a consideration of the various attempts to establish constants by which organic carbon can be multiplied to give organic content values, including those of the present study, it became clear that all values for organic content established in all work past and present are at best only interpretive rather than absolute.

The Range of Organic Content: The organic content in the bottom sediments of the surveyed portion of Boston Bay were found to range between 0.22% and 11.7% (Table 6). The majority of the values, however, are below 2%. A few high values occur only in the uppermost layers of six specific areas, localized in Boston Bay as follows: (1) 3 miles northeast of Deer Island, (2) 1 mile east of the seaward end of North Channel, (3) just north of The Graves, (4) just southeast of Marblehead Channel, (5) off the east shore of Nahant, and (6) nearly 10 miles east of The Graves.

The Origin of Organic Content in Boston Bay: The source of organic matter occurring in the Boston Bay bottom sediments is believed to be derived from populations of marine phytoplankton (Emery & Rittenberg, 1952; Riley, 1941; Zobell, 1946). Organic residues which result from the degradation of the original source materials by way of the food chain are ultimately

Table 5

Organic content data from sediments of Buzzards and Cape Cod Bays computed by loss of weight on ignition (after Waksman, 1933)

Sample Number	% Weight Loss on Ignition	% Organic Carbon	% Organic Carbon of Organic Content
1 2 3 4 5 6	7.65 1.85 5.25 5.90 7.45	3.37 1.21 0.58 1.76 1.96 2.30	44.0 34.6 31.4 33.6 33.2 30.9

mean = 34.6 % Carbon

Range of organic carbon:

Euzzards Bay sediments 1.21% to 3.37% Cape Cod Bay sediments 0.34% to 2.75%

Organic content, median diameter of sediments, and rigidense values obtained from sediments from Boston Bay

Station-Core Number	Depth of Sample from Top of Core	Median Liameter of Sediment in mm	Type of Sediment	% Organic Carbon (Allison Method)	% Organic Content (Present Study) X Factor 2.29	% Organic Content (Trask) X Factor	% Organic Content (waksman) X Factor 1.887	% Organic Content (Boysen-Jensen) X Factor 2.0	Rigidense cm/2 mins.
132A 132A 133B 133B 134A 134A 134B 134B 148A 148B 148B	0' 1.5' 0' 2' 3.5' 0.5' 3.5' 0' 0' 0' 1'	0.022 0.0026 0.051 0.0026 0.018 0.291 0.125 0.003 0.002 0.312 0.006 0.190 0.045	Silt Clay Silt Clay Silt Sand Clay Clay Sand Silt Sand Silt	2.02 0.507 0.984 0.40 0.047 1.025 0.478 0.443 0.227 3.55 2.98	4.64 1.16 2.25 0.92 1.48 2.35 	3.46 0.86 1.67 0.67 1.10 1.74 0.81 0.75 0.39 6.04 5.07	3.84 0.96 1.86 0.76 1.19 1.94 0.90 0.84 0.43 6.70 5.62	4.04 1.01 1.97 0.80 1.30 2.05 0.96 0.89 0.45 7.10 5.96	525251 21353
*1480 **1480 152A 152B 152B 152C 152D 152E 152E 153A	1.55.0254.6890	0.037 0.217 0.054 0.002 0.044 0.002 0.003 0.003 0.020 0.022	Silt Sand Silt Clay Silt Clay Clay Clay Silt Silt	1.431 0.599 1.361 0.463 0.513 0.580 0.504 0.264	3.28 1.37 3.12 1.06 1.17 1.33 1.15	2.44 1.02 2.32 0.79 0.87 0.99 0.86	2.70 1.13 2.68 0.88 0.97 1.09 0.95	2.86 1.20 2.82 0.93 1.03 1.16 1.01	3.7 15.5 2.2 2.4 1.3 2.5 5.5

Note: Column 6 gives organic content values computed from the factor 2.9 derived from the present analysis; Column 7 values computed from Trask's factor 1.7; Column 8 values computed from Waksman's constant 1.887; and Column 9 values computed from Boysen-Jensen's factor 2.0.

- * Samples containing coal fragments
- ** Samples from cores believed to be disturbed during coring operations.

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Table 6 (cont'd.)

153B	21	0.002	Clay	0.35	0.803	0.59	0.61	0.70	1.9
153B	31	0.047	Silt						
1530 153D	5.5'	0.004 0.002	Silt Clay	0.414	0.95 1.01	0.70		0.83 0.88	2.3 1.8
153D	5.5 61	0.002	Clay						1.0
153D	7.5!	0.0015	Clay	0.375	0.860	0.64	0.71	0.75	1.8
154A 154B	0 ' 2 '			2.56 0.724	5.86 1.66	4.35	4.83	5.12 1.45	5.5 0.1
154C	41		Silt	0.541	1.24	0.92	1.02	1.08	1.1
154D	61	0.0031	Clay	0.313	0.72	0.53	0.59	0.63	2.3
154E	81		•	0.407	0.93	0.69	0.77	0.81	2.2
155A	01		Sand	1.82	4.16	3.09	3.44	3.64	
155A 162A	1' 0'	0.056 0.083	Silt Sand	0.454	1.04	0.77	0.85	0.91	2.9
162A	1.5'		Clay						_ ,
162B	21	0.0501	Silt	0.502	1.15	0.85	0.94	1.05	3.9
162C	4!	0.0037	Clay	0.449	1.03	0.76	0.85	0.90	1.2
**163A	0' 1'		Clay	1.83	4.19 0.78	3.10 0.56	3.45	3.66 0.68	5.5 0.6
*163A **166A	01	0.144 0.017	Sand Silt	0.339 5.13	11.73	8.70	9.65	10.03	5.5
**166B	Ž١	0.252	Sand	0.215		0.37	0.41	0.43	1.2
**169A	0 '	0.0013	Clay	3.68	8.44	6.25	6.95	7.35	5.5
169A	0.5!	0.002	Clay				7 09	2.10	2 7
169B 169C	21 Jul	0.176 0.059	Sand Silt	1.05 0.856	2.41 1.98	1.79 1.47	1.98 1.66	2.10 1.76	3.7 2.2
169D	4!	0.013	Silt	1.35	3.10	2.30	2.54	2.70	1.6
1 69 D	81		Sand	1.23	2.82	2.10	2.32	2.46	2.4
170A	01	1.42	Sand	0.632	1.45	1.08	1.19	1.27	1.2
170B	21	0.0069	Silt	0.736	1.69	1.25	1.38	1.47	2.9
**173A **173B	0' 1'	0.0034 0.233	Clay Sand	2.63 0.149	6.03 0.34	4.52 0.25	5.0 0.28	5.32	5.5
174A	01	0.081	Sand	0.213	0.49	0.36	0.42	0.43	2 2 . 6
171A	1.5'		Sand						_ • -
174B	21	0.0014	Clay	0.415	0.95	0.71	0.78	0.83	0.5
**175A	01		Sand	0.094	0.216	0.16	0.18	0.19	5.0
178A 178A	0' 1.5'	0.026 0.015	Silt Silt	1.85	4.24	3.14	3.47	3.70	5.5
##178B	2.51	0.041	Silt	1.19	2.73	2.01	2.24	2.38	2.0
* *178B	51	>4	Gravel	1.22	2.80	2.08	2.30	2.44	3.0
179A	0'	0.071	Sand	1.18	2.70	2.0	2.22	2.36	45555555555555555555555555555555555555
179B 180A	21 01	0.071 0.027	Sand Silt	0.591	1.35	1.01 5.50	1.12 6.10	1.18 6.44	5.5
183A	0'	0.0097	Silt	3.22 4.05	7.38 9.28	6.80	7.55	8.0	5.5
**184A	01	0.026	Silt	4.09	9.37	6.95	7.72	8.18	5.5
187A	0'	0.112	Sand	0.123	0.282	0.21	0.23	0.25	1.5
188A	0'	0.012	Silt	3.45	7.91	5.86	6.50	6.90	5.5
189A 189B	01 21	0.013 0.029	Silt	1.53	3.51	2.60 4.15	2.88 4.60	3.06 4.88	5.5
1896 1890	41		Silt Clay	2.44 0.219	5.60 0.50	0.37	0.41	0.434	2.6
192A	Ŏ'	0.051	Silt	0.91	2.09	1.55	1.74	1.84	4.35
192B	21	0.139	Sand	0.314	0.72	0.53	0.59	0.63	2.15

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Table 6 (contid.)

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Table 6 (cont'd.)

226A 226B 227B 227B 228B 228B 228B 228B 228B 228	0 2 4 0 2 5 0 2 0 5 0 2 0 5 0 2 4 0 2 4 0 2 5 0 2 0 2 0 2 0 2 0 5 0 5	0.059 0.050 0.050 0.067 0.079 0.094 0.0013 0.0013 0.0073 0.0013 0.0013 0.00	Sand Sand Sand Sand Sand Sand Sand Sand	0.536 0.625 0.775 0.4775 0.5994 0.5594 0.489 0.555 0.456 0.66	1.782 1.782 1.782 1.898 1.944 1.945 1.	0000100010097254172 956459700097254172 956459700097254172 96682913974046 97884172 978882913974046 97884172 978882913974046 978882913974046	1000101010101010111121111101110011504 011	1.69 1.69 1.69 1.69 1.68 1.19 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1.01 1.00 1	330523304005055311200304322124515 252
2458 2458 246A 246A 2165 249A 2498 **251A	0. 2. 4. 0. 0. 2.	1.497 1.57 0.152 0.140 0.126 0.047 0.003	Sand Sand Sand Sand Sand Silt Clay	0.66 0.995 0.997 0.521 0.525 0.531 0.267 2.67	2.28 2.28 1.19 1.20 1.22 0.61 6.11	1.12 1.69 1.70 0.89 0.90 0.91 0.45 4.54	1.25 1.88 1.88 0.98 0.99 1.00 0.49 5.04	1.32 1.99 1.04 1.05 1.06 0.53 5.34	53236525
							*		

dispersed by tidal currents in the same manner as the coastal transport and deposition of fine-grained sediments. Little organic matter is attributed to that transported by river and sewage effluents, except in extremely localized areas near such effluent outlets. (Crosby, 1907; La Forge, 1932; Twenhofel, 1950; and others).

The Nature of Organic Residues in the Boston Bay Sediments: Twenhofel (1950, p. 470-471), Zobell (1946), and others state that recent organic residues found in freshly deposited marine sediments of an estuarine-like environment are ligno-proteins hemicelluloses, and perhaps gums, which are acted upon chiefly by bacteria in fairly well aereated surface layers of the sediments. In time as sedimentation proceeds, these compounds change more and more to waxes, fats, and resin-like organic residues which are oxygen low and carbon rich in constitution. The trend is toward an increase in the ratio of carbon to total organic content. Trask is in agreement with this contention and uses a constant of 1.7 for recent sediments with a lower carbon content, and 1.5 for ancient sediments with a higher carbon content. Waksman has shown what organic compounds are likely in such residues for sediments analyzed in his laboratory (Waksman, 1933). Twenhofel refers to an analysis by David White regarding aging of organic residues in sediments (Twenhofel, 1950, p. 481). Boysen-Jensen was more concerned with the organic carbon content of living plant tissues (the marine phanerogam, Zostera), which he assumed was the chief source of organic content in estuarine environments. He established values for vascular plant detritis and extrapolated for those in sediments (Boysen-Jensen, 1941). Considerable information can be found in the literature of biochemistry dealing with the problem.

Even though it is recognized that such organic residues do exist in sediments, and something is known concerning their chemical nature, it should be clearly understood that the whole question of establishing values for organic content, let alone the kinds of organic matter in sediments, is based upon a number of assumptions not yet supported by sufficient evidence. For this reason, Trask (1942) preferred to discuss organic content in terms of organic carbon per se. The discussion that follows in this present study should be seen in the light of these circumstances.

The mean carbon content and the spread of values obtained from the Boston Bay sediments is indicated in Figure 2, where they are compared to mean analyses of other sediments and to the carbon contents expected for a variety of types of organic material associated with organic deposits. The source materials and direction of reduction are also suggested to indicate the gradual transition of low carbon compounds to high carbon

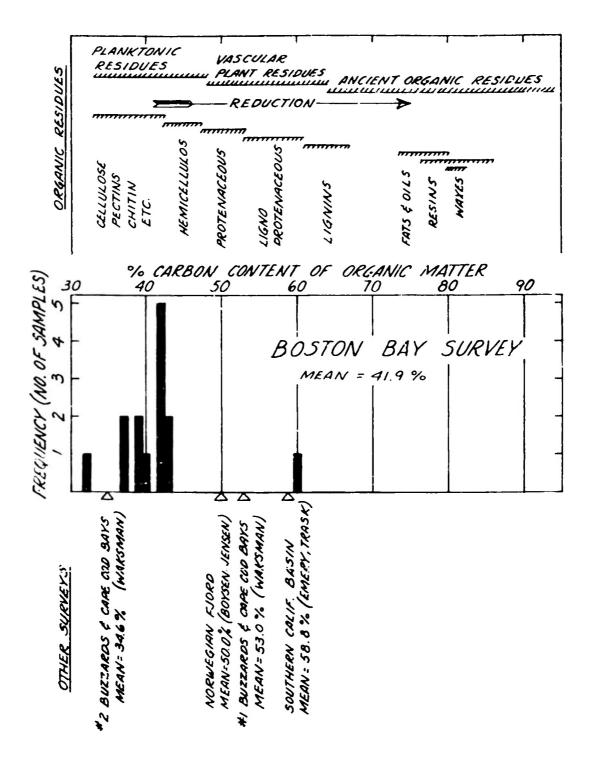


Fig. 2 % Carbon content of organic matter and possible organic residues they represent in Boston Bay and other surveys.

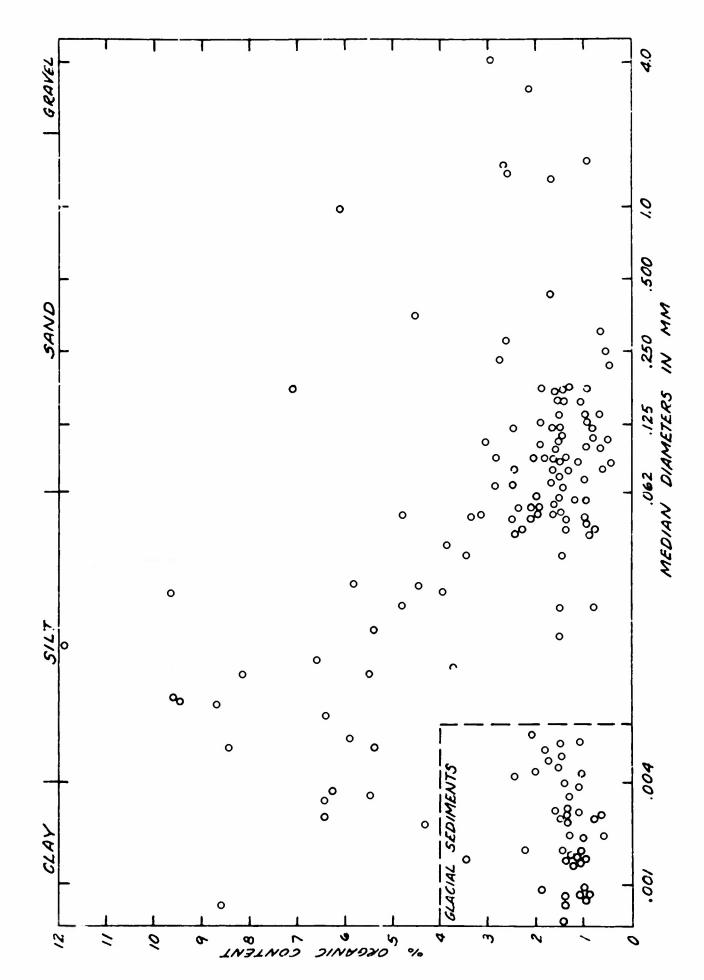
compounds in time with depth and other changes in the sedimentary environment.

If the methods for carbon analysis were comparable the carbon of the organic residues in the Boston Bay bottom sediments is not reduced to the same degree as in the sediments studied by Trask, Emery, Waksman, and Boysen-Jensen in other environments. The scatter of carbon values suggests that the Boston Bay sediments have mostly hemicellulose-like rather than proteinaceous, ligno-proteinaceous, or waxy-resinlike residues. The presence of hemicelluloses and similar carbohydrate-like compounds suggests organic materials which have undergone little degradation and are more nearly related to phytoplankton residues.

Organic Content and its Relation to Sediment Stability: It was the object of this study of organic residues to relate the types of organic materials involved to the effects they produce on the physical qualities of sediments. A comparison of the organic content data with the field data for the Boston Bay area shows a qualitative correlation with rigidense and grain size. Although there is likewise some qualitative correlation with water content and bulk density, these latter factors are believed to be expressed by the rigidense values (C.B.I. Ref. No. 52-24). Data from the Boston Harbor inshore Survey supports this contention to a limited extent (w.H.O.I. Ref. No. 52-56).

The higher values of organic content in all cases are associated with fine fractions of sediment (w.H.O.I. Ref. No. 53-17); namely, the silts and clays (Fig. 3). This fact is not only borne out in the data obtained from Boston Inshore Survey, but also is supported by the work of Trask (1942), Emery and Rittenberg (1952), Waksman (1933), and others (Twenhofel, 1950).

Although clays exposed on the harbor bottom occasionally reached 6% organic content, most clays which are believed to be of glacial origin occur below the surface and values range from 0.7% to 1.6% generally (see box in left-hand corner of Fig. 3). The highest values for organic content were obtained in silts and clays in the superficial layer of sediments in certain areas. Such values obtained ranged from 4% to 11.7%. Organic content occurring in silts at depth was relatively low, mostly less than 2%. Sands and coarser sediments, especially those free of any fine-grained fractions, contained the lowest percentages of organic content, ranging mostly below 1% and including the lowest values obtained (Table 6, and Fig. 2).



Organic content velues compared with the median diameters of sediment particles. Fig. 3

Rigidense values show a positive covariation with organic content in this present survey. The higher the rigidense the higher the organic content, generally. As there is some increase both in rigidense values and organic content with decrease in grain size, the increase in rigidense might not be caused by the higher organic content. However, a study of the relationship between rigidense and grain size did indicate that other factors might be operating which affect the stability of sediments as measured with the rigidense instrument (C.B.I. Ref. No. 52-24). Since the presence of colloidal particles of organic matter in a clay is known to increase its plasticity, it has been assumed that organic content is an important modifying agent affecting the stability of fine-grained sediments (Taylor, 1948, pp. 378-379).

- J. J. Donahue has carried out some experiments on marine sediments from Narragansett Bay and littoral sediments from the coast of Maine and the affects of hemicellulose-like organic compounds in reducing shearing strength, and reports the following from his unpublished work.
 - (1) Hemicellulose-like residues have been observed as a constituent part of recent marine sediments;
 - (2) In certain samples it was observed that under the circumstances of certain environmental factors which support oxidation in favor of reduction, hemicellulose-like organic residues can account for the major portion of the organic content of the sediment;
 - (3) It was demonstrated in the laboratory that samples containing natural water and hemicellulose-like residues as an integral part of the sediment composit show less resistance to penetration than do the same samples without the residues, but where the natural water content has been kept essentially the same.
- J. J. Donahue's observations tend to support the findings of this present survey with respect to the kinds of residues present in the marine sediments of the region. He also offers evidence for a direct correlation between loss of shearing strength and the presence of hemicellulose-like residues in a sediment.

Organic Content and the Sedimentary Environment: The highest values for organic content obtained in this survey in Boston Bay were always associated with accumulations of

^{*} Personal correspondence from J. J. Donahue, March 18, 1953.



fine-grained sediments and usually high rigidense values. At depths of 2 and 4 feet, respectively, Kullenberg cores provided samples indicating what may have been old deposition areas for fine-grained sediments shown by the presence of organic content in excess of values in the adjacent vicinity. Often such old regions of silt deposition which may have been in existence several thousands of years were located near, but somewhat displaced from, recent surface silt deposition areas, suggesting that the coastal topography of the region had been modified in more recent times (Fig. 4A, E).

In this survey some knowledge of the higher values of organic content in the profile of bottom sediments has provided a helpful clue in the location of the more unstable sediments occurring in the Boston Harbor approaches. Conversely, areas with low values for organic content tend to support evidence suggesting more stable areas in the bottom sediments of this region.

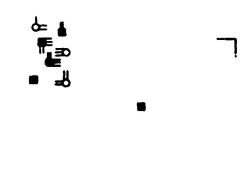
Surface samples from the Kullenberg cores give some evidence of local sewage effluent pollution of the fine-grained surface sediments near sewage outlet sources. The lowest organic content values occur between and beyond such effluent outlets. The very highest values for organic content in surface sediments occur near the northeest end of North Channel near the Deer Island sewage outlet. Organic content values range from 11.7% at the northeast end of the channel (station 166) **, to 6.01% (station 121) at the seaward extension of this local region where high values of organic content occur. Beyond and to the seaward of this area delimited to the northeast of North Channel (Fig. 4A, B, Table 6), organic content values in the surface sediments drop off rapidly to 1.8% or less. Data from stations 166, 183, 186, 186, and 184 near the end of North Channel are lacking at 2 and 4 fcot levels, but cores from stations 221, 189, 219, 169, and 178 in the same vicinity imply that this deposition area is probably one of considerable age. However, considering the possibility of this region being subject to the dumping of refuse and channel dredgings, the above conclusions may be unjustified.



^{*} The location and number for stations in Boston Bay from which Kullenberg cores were obtained are given in W.H.O.I. Ref. No. 52-56.

^{**} Station 166 lies inside the region within which bacteriological analysis reports a 90% positive count of Coli-Aerogenes group bacteria from a 0.1 cc portion of sea water (Commonwealth of Mass., 1937).

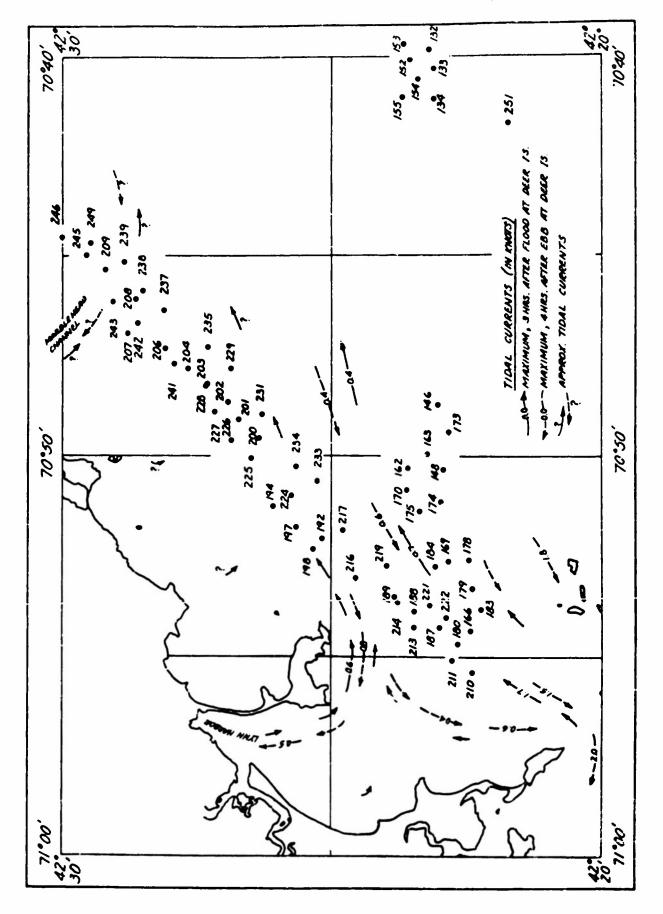
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PERCENT

The distribution of organic content in Boston bay. Pic. 4h.



Location of Kullenberg core stations in boston Bay. F18. 4B.

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An ancient deposition area is suggested east of the North Chennel entrance in the vicinity of The Graves (stations 169 and 178). The organic content and rigidense values are somewhat higher at all core levels sampled than those for the surrounding area.

About two nautical miles to the northeast of North Channel another old region of deposition is suggested at a depth of 2 feet, but not at 4 feet (stations 214, 189, and 216). Deer Island was cut off from the mainland until 1936 (Nichols, 1948) and a ship channel from the Mystic and Charles Rivers delta area opened over a sill through which tidal currents passed. The so-called settlement area lies in the path of what was probably a former track for tidal currents passing to and from the sill. At the junction of this tidal stream with another coursing around the southeast end of Nahant Peninsula entering the Saugus River estuary, a check in current velocity may have occurred over this so-called deposition area, contributing to its sedimentation. The low values for organic content at a depth of 4 feet would suggest that the deposition of fine-grained sediments took place only over a limited period of time in the area.

Where strong tidal currents enter and leave the Saugus River estuary in the vicinity of the Lynn sewage outlet in contact with a slower moving mass of water in Nahant Bay, surface sediments contain organic content values between 4.0% and 7.0% (stations 197 and 233). Rigidense values are likewise high for the immediate area delimited. To the northeast of the surface area just described, at depths of 2 and 4 feet, the concentrations of organic matter are generally higher than those for the surrounding area at those levels, ranging from 1.3% to 3.0% (stations 224 and 234). It might be assumed that this history of this particular deposition area has been a long one, even though the superficial deposition area has been shifted to the southwest, due possibly to changes in the coastal topography.

What may be presumed to be an area of deposition was noted just seaward to the southeast of Marblehead Channel. Values for organic content range from 4% to nearly 6% in the surface layer of silt (stations 242, 243, and 208). Rigidense values are correspondingly high. At a depth of 2 feet the low organic content values indicate that the immediate area has not been long an area of deposition. However, what may be an ancient subsurface deposition area is indicated by a group of three cores obtained from sediments to the south of the surface region of deposition just described (stations 237 and 235). The organic content values range between 1.5% and 2% in this area, even at the 4 foot level. Although

such evidence might suggest that earlier this was an area subject to the deposition of fine-grained sediments, the relative amounts of organic matter found in this part of Boston Bay is small in contrast to values observed in other merine sedimentary environments such as the Gulf and California coasts (Trask, 1942; Emery & Rittenberg, 1952).

A grea of deposition just north of The Graves is suggested in the station group including 148, 163, and 173, the uppermost layers of which contain organic content values ranging from 4.19% to 8.15%. High rigidense accompanies these values.

A region of deposition is inferred by organic content analysis at the end of the eastern leg of the R/V CARYN's coring operation (stations 155, 154, 152, and 132). It should te mentioned that station 155 is on a considerably higher rise of the bottom than the other three stations mentioned and may not be related to them. Apparently a surficial layer of sediment occurs in this area, having a range of organic content values between 4% and 6%. The area may be considered to be safely beyond the influence of sewage effluents by virtue of its distance from such sources and the nature of the tidal circulation pattern over the region (U. S. Dept. Comm., U. S. C. & G. S. Serial #504). Such being the case, the amount of organic content may be considered to be the result of natural sedimentary agencies uninfluenced by the activities of man. The subsurface sediments contain organic content values at the 2 and 4 foot levels, indicating that presumably sedimentation processes depositing silts and clays have been in progress over several thousands of years. Three of the five cores obtained had organic content values over 1% in contrast to values ranging less than 0.5% in the subsurface layers adjecent to the so-called deposition area. Despite the assumed length of time involved, the sedimentation rate has been moderate as indicated by the rather low level of reduction of organic residues shown in the analysis. Rigidense values ere moderate for the subsurface layers, suggesting that the plasticity of fine-grained sediments present are not seriously affected by organic content.

High values for organic content were noted for stations 251 and 245. However, as there were no other stations in their immediate vicinity with corresponding values, no conclusions are attempted regarding their significance.

A general statement with regard to organic content in the fine-grained sediments of the Boston Bay area should emphasize the fact that organic content values only approached what are believed to be critical values in the immediate superficial layers of a few isolated areas described. The extent of weakening of a fine-grained sediment by the presence of organic content in quantity is undetermined as rigidense values in the more critical cases were beyond the scale of the rigidense instrument much of the time. However, such critical areas were shown never to exceed 2 feet in thickness. In contrast to the organic content of marine sediments in silt and clay-filled basins off the Gulf states and California coast, even the highest values obtained in this inshore survey of the Boston Bay region were in general significantly lower (Emery & Rittenberg, 1952; Trask, 1939, 1937, 1934, 1933; Waksman, 1933)*.

Although the environment of the sediments studied by Waksman compare favorably with those of the present study, the environments of the sediments studied by Trask in the Gulf states and Southern California offshore regions were generally farther from shore and in deeper water. Perhaps a more realistic comparison of data may be made when the results from the present survey are studied along with those from other inshore programs now in progress.

^{*} Emery reported a median of nearly 6% organic content with a few high values, ranging from 8.5% to nearly 11.0%, for inshore sediments of the Southern California basin, at a depth of 3 inches below the surface layer.



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SUMMARY

An analysis and study of the significance of organic content in sediments of Boston Eay was undertaken as part of the Inshore Survey Program.

- An analysis was made for organic carbon using Allison's modification of Schollenberger's chromic acid reduction method for the determination of organic carbon in soils. Application of the method to marine sediments required some further mod1fications; namely, a careful sample preparation schedule, a longer digest period at constant temperature, the addition of silver sulfate, and a need for iron analysis to determine if it were present in concentrations which would interfere. the case of the Boston Bay sediments, iron content was found to be low and its effect upon the analysis was considered negligible. It was felt that no correction was necessary for salt error using the silver sulfate. It was found unnecessary to use a Kipp generator to provide a hydrogen atmosphere over the ferrous ammonium sulfate solution as its stability was satisfactory for the duration of each preparation of the reagent. An increase in acidity of the reagent seemed to favor its stability.
- 2. The Allison method is not an accurate means of obtaining absolute values for organic carbon, a fact recognized by Emery, Trask, and others. The method has the inherent weakness of reflecting the state of reduction of a number of soil constituents other than organic carbon, depending largely upon the specific conditions in the environment. Only relative values or reduction numbers can be obtained with this technique.
- 3. To establish a constant by which organic carbon could be referred to total organic content values, total organic matter analysis was made on 8% of the samples by weight loss on ignition. The mean percentage of organic carbon was computed as 41.9% of the total organic content; hence the mean organic content is 2.29 times the organic carbon value. The organic content values obtained in the present analysis were computed by multiplying values for organic carbon by 2.29.
- 4. Organic matter deposited in the sediments of Boston Bay is believed to be derived largely from marine sources, the most important of which are the populations of phytoplankton in coastal waters.
- 5. Organic content in Boston Bay ranges from 0.215% in coarse sands to 11.7% in fine silts; but the majority of values are below 2% and occur in various grades of sands.

- 5. As the average percentage of organic carbon was computed as 41.9% in the Boston Bay sediments, it is implied by interpretation that mostly hemicellulose-like organic residues occur in the sands, silts, and clays. Unpublished data from another study shows that significant amounts of hemicelluloses occur in marine sediments, and do influence the plasticity of sediments. Studies by Trask on sediments offshore from the Gulf states and Southern California, and by Boysen-Jensen in those from a fjord in Norway, suggested that more highly reduced organic residues occurred in the sediments of those regions in contrast to those of the Buston Bay area. The possible inference is that the Boston Bay finegrained sediments may have been deposited more rapidly. In addition there is the suggestion that the high percentage of organic content reported by these investigators for their respective studies mentioned above might indicate that there was possibly a greater accumulation of fine-grained sediments in those environments than in the Boston Harbor area. study of sediments in Buzzards and Cape Cod Bays tends to support the present analysis, providing one uses his weight loss on ignition values for total organic matter.
- 7. A positive covariation was noted among higher organic content and high rigidense values and small grain sizes. The smaller the grain size and the more plastic the sediment, the higher the organic content generally. For a given grain size, organic content decreased gradually with depth.
- 8. An analysis of organic content with respect to field positions and depths of the samples provided some suggestion as to regions of recent or more ancient or long-standing sedimentation in the same localized deposition areas where fine-grained sediments have accumulated. These areas, including both recent and ancient deposits of fine-grained sediments, are localized in Boston Bay as follows: (1) 3 miles northeast of Deer Island, (2) 1 mile east of the seaward end of North Channel, (3) just north of The Graves, (4) just southeast of Marblehead Channel, (5) off the east shore of Nahant, and (6) nearly 10 miles east of The Graves.

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